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Bio-directed one-pot synthesis of Pt-Pd alloyed nanoflowers supported on reduced graphene oxide with enhanced catalytic activity for ethylene glycol oxidation

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ABSTRACT

Amino acids with intrinsic affinity to metallic ions can be employed for controllable synthesis of metal nanocrystals with tunable size and morphology, as well as less toxicity. In this work, *L*-histidine was exploited as a structure-director for *in situ* controlled growth of bimetallic PtPd alloyed nanoflowers on reduced graphene oxide (RGO-PtPd nanoflowers) by a simple one-pot aqueous approach at room temperature. There was no seed, template, special apparatus or organic solvent involved in the synthetic process. The as-synthesized nanocomposites displayed improved electrocatalytic ability and durability for ethylene glycol oxidation reaction (EGOR) as compared to Pt-RGO, Pd-RGO, commercial PtRu/C, Pt black and Pt/C catalysts.

1. Introduction

In last two decades, fuel cells are extensively investigated in many energy applications owing to their high energy efficiency, low environmental footprint, and gentle reaction conditions [1,2]. Amidst much progress, however, there are several problems such as the high volatility and toxicity of methanol in direct methanol fuel cells (DMFCs) [3], which may cause some troubles when DMFCs are applied in consumer electronics [4]. Unlike methanol, ethylene glycol (EG) is a good candidate thanks to its high boiling temperature, vapor pressure, and energy density, along with low toxicity [5]. Furthermore, EG can be easily produced from biomass and automated production [6].

Pt-based bimetallic alloys have demonstrated the enhanced electrocatalytic performances in contrast to their individual counterparts [7], owing to the synergetic effects (including bifunctioncal and electronic effects) between the two metals. The bifunctional effects endow the efficient adsorption of the OH_{ad} species and complete removal of the adsorbed carbon oxide (CO_{ad}) to improve the catalyst stability [8]. And the electronic effects can facilitate the electron transport between the two metals to increase the electrocatalytic performance [9]. To date, several Pt-based catalysts were prepared [10] (e.g., PtSn [5], PtRu [9], PtPd [11], and PtAu [12]) with the improved electrocatalytic performances for alcohol oxidation reactions.

As manifested, the enhanced catalytic performances of PtPd nanocatalysts for alcohol oxidation is ascribed to the stronger tolerance of Pd toward CO_{ad} poisoning [13] and more abundant reservation with 50 folders higher relative to Pt. Moreover, the shape and size of Pt-based architectures have great effects on their catalytic property [14]. For example, nanoporous twinned PtPd possesses highly catalytic activity and stability toward methanol oxidation [15]. In another example, three-dimensional Pt-Pd alloyed multipods were synthesized by a facile one-pot solvothermal method [16]. Nevertheless, the mentioned methods suffer from relative high reaction temperature, long time operation and toxic agents used [17].

Many supports especially graphite have been employed to endow the above catalysts with well distribution [18], because of their enlarged surface area, good electrochemical stability, high electrical conductivity, and strong adhesion to the catalysts [19]. For instance, the surface area of Fe_3O_4 nanoparticles/RGO is 192 $m^2 g^{-1}$, which is larger than that of pure Fe_3O_4 nanoparticles [20], revealing the increased surface area of the resulting nanocomposites and the decreased dosage of the catalysts [21].

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This is mainly attributed to the abundant oxygen-functional groups on reduced graphene oxide (RGO) surfaces (e.g., epoxy, hydroxyl and carboxyl groups) which can provide more active sites available for the catalysts [22].

In this work, RGO supported PtPd nanoflowers (RGO-PtPd nanoflowers) was synthesized in the presence of *L*-histidine at room temperature. The catalytic ability of the as-synthesized nanocomposites was tested in 1.0 M KOH, using ethylene glycol oxidation reaction (EGOR) as a model system.

2. Experimental

2.1. Preparation of RGO-PtPd nanoflowers

Before use, GO was prepared by the modified Hummer's method [23]. For preparation of RGO-PtPd nanoflowers, 0.50 mL of H_2PdCl_4 (100 mM), 1.30 mL of H_2PtCl_6 (38.62 mM), 38.8 mg of *L*-histidine, 25 mg of polyvinyl pyrrolidone (PVP), 2.0 mL of GO, and 6.21 mL of water were subsequently put into the vessel under vigorous stirring for 0.5 h, followed by adjusting the pH value within 11~12 with 0.1 M NaOH. Afterward, 100 μL of hydrazine (16.41 M) was injected into the mixture and reacted at 25 °C for 1 h under stirring. The precipitates were thoroughly washed with water and ethanol for several times to remove the residual PVP. Chemicals and detailed characterization sections were provided in Supporting Information (SI).

In control experiments, Pd-RGO and Pt-RGO were prepared *via* only using H_2PdCl_4 or H_2PtCl_6 as the precursor, respectively, while the total precursor concentrations were kept unchanged.

2.2. Electrochemical measurements

In electrochemical measurements, a three-electrode system was used. For the construction of RGO-PtPd nanoflowers modified electrode, 1 mg of the sample was mixed uniformly with 1 mL of water by ultrasonication (1 mg mL^{-1}). Next, 6 μL of the mixture was dropped onto the surface of GCE and dried naturally, followed by casting 6 μL of Nafion (0.05 wt%) on the electrode surface. The resulting electrode was named as RGO-PtPd nanoflowers/GCE.

In control experiments, commercial Pt black, PtRu/C, Pt/C (50 wt%), Pd-RGO and Pt-RGO modified electrodes were fabricated in the similar way, denoted as Pt black/GCE, PtRu/C/GCE, Pt/C/GCE, Pd-RGO/GCE and Pt-RGO/GCE, respectively. The loadings of the catalysts modified electrodes stated in this work are all 0.085 mg cm^{-2}, respectively.

Electrochemically active surface area (ECSA) of RGO-PtPd nanoflowers/GCE was calculated based on the CO_{ad}-stripping voltammograms recorded in 0.5 M H_2SO_4, based on the integration of the consumed charges during the CO_{ad} stripping after correction for the double layer and anion adsorption related currents [24]:

$$\mathrm{ECSA}\ (\mathrm{m^2\,g^{-1}}) = Q_{CO}/(m \times Q_0)$$

where Q_{CO} is the integrated consumed charges during the CO_{ad} oxidation, Q_0 is the standard charges required for the oxidation of CO_{ad} monolayer on Pt surface with the value of 420 μC cm^{-2} and *m* is calculated based on the experimentally (TGA and EDS) determined metal loading.

Cyclic voltammetry and chronoamperometry experiments were conducted to investigate the electrocatalytic performance of RGO-PtPd nanoflowers/GCE in 1.0 M KOH containing 0.5 M EG.

3. Results and discussion

3.1. Characterization of RGO-PtPd nanoflowers

TEM images show the morphologies of RGO-PtPd nanoflowers (Fig. 1). There are a lot of well-defined PtPd nanoflowers dispersed uniformly on RGO surfaces (Fig. 1A and B) with the size mainly located in the range of 30 ~ 45 nm (inset in Fig. 1A). HRTEM image in the marked section reveals more detailed structural characters

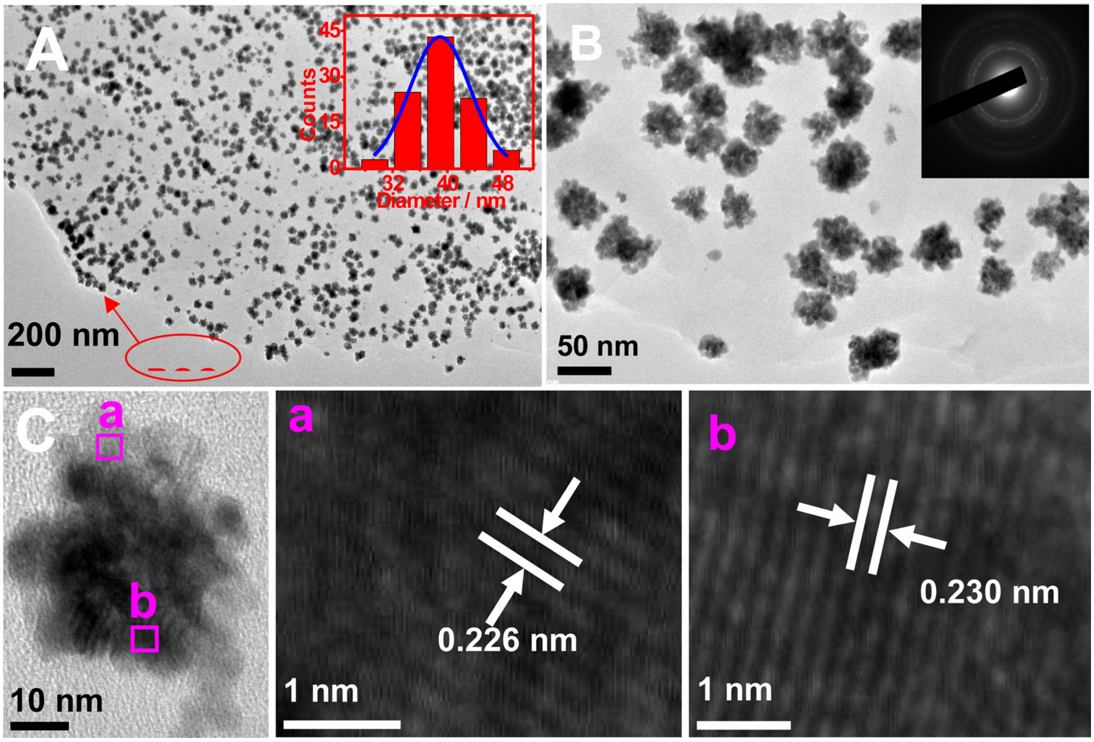

Fig. 1. Low (A), medium (B), and high-resolution (C) TEM images of RGO-PtPd nanoflowers. Insets show the particle size distribution in Fig. 1A and SAED pattern in Fig. 1B, respectively.